Transition metal oxides - Multiferroics go high-T-C

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TRANSITION METAL OXIDES

Multiferroics go high-T_C

The discovery of magnetically induced electric polarization in cupric oxide at 230 K has uncovered a new class of multiferroics with significantly higher ordering temperatures.

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The discovery by Tsuyoshi Kimura and colleagues of a multiferroic coupling in cupric oxide up to 230 K, as reported on page 291 of this issue[1], is all the more remarkable as physicists had been wondering for a long time if it is possible at all to align electric dipoles by magnetic fields or change the direction of magnetization by applying voltage. To some, such a magnetoelectric coupling may seem to be an oddity, as static magnetic and electric dipoles do not interact. Others may find it to be the most natural thing in the world, because electrons responsible for physical properties of solids carry both charge and spin. But the fact is that until recently the number of known materials showing pronounced magnetoelectric effects was very small.

However, the situation changed when in 2003, Kimura *et al.* found that magnetic ordering in $TbMnO_3$ induces electric polarization[2], which soon led to the discovery of a dozen similar materials — called multiferroics, as they are both magnetic and ferroelectric[3]. The direction of the electric polarization vector and dielectric susceptibility of these materials can be very efficiently controlled by applied magnetic fields.

The discovery of this magnetically induced ferroelectricity helped to resolve an old problem of chemical incompatibility in the attempts to simultaneously realize ferroelectric and magnetic orders, which for many years hampered the progress in the search for multiferroics. There are still a few hurdles left on the way to practical applications of these materials: small values of induced electric polarization and low transition temperatures, which, with one exception[4], are limited to 40 K.

The discovery that cupric oxide (CuO, also known as tenorite) is a multiferroic material with a high antiferromagnetic transition temperature T_N of 230 K therefore represents a significant advance. However, this finding doesn't seem accidental in light of the fact that CuO is also the starting material for the synthesis of copper-oxide-based superconductors, which twenty years ago broke 'the theoretical upper bound' on superconducting transition temperatures.

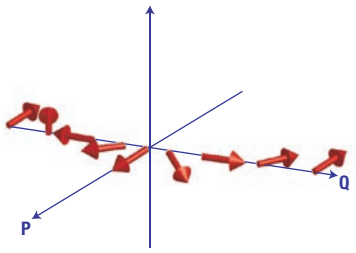

Figure 1 Spin spiral structures — which often arise out of geometric frustration that makes simple collinear orderings impossible — can induce an electric polarization. This polarization, **P**, lies in the plane of the spiral, but perpendicular to its propagation vector **Q**.

At temperatures below 230 K, CuO shows antiferromagnetic order, and, as for most of the recently discovered multiferroics, spins in the ferroelectric state of CuO form a periodic spiral superstructure between 213 and 230 K (Fig. 1). Here, electric polarization is induced in the plane of the spin spiral, but perpendicular to the spiral's wave vector. If the temperature is dropped below 213 K, the spiral ordering is replaced by a collinear spin structure, and the electric polarization disappears.

The origin of spiral ordering was first discussed fifty years ago and two alternative explanations were proposed. One, put forward by Villain[5], Kaplan[6] and Yoshimori[7], is based on magnetic frustration, where geometric constraints and competing interactions make it impossible to select a single lowest-energy configuration of collinear spins. In this situation, spiral ordering emerges as a compromise. Another idea was proposed by Dzyaloshinskii, who noticed that the free energy of magnets without inversion symmetry can have a phenomenological term that is the source of inhomogeneous magnetic order[8]. Its microscopic origin was elucidated by Moriya, who showed that relativistic corrections led to a new interaction that favoured non-collinear spins[9]. In the course of time both these explanations were proved to be right: there are many frustrated magnets showing spiral spin ordering and there are materials, such as ferroelectric $BiFeO_3$, where the breaking of inversion symmetry transforms a uniform antiferromagnetic state into a low-pitch spin spiral.

In spiral multiferroic materials these two mechanisms work together. Frustration induces spiral ordering, which breaks inversion symmetry. This activates the Dzyaloshinskii–Moriya interaction, which forces positive and negative ions to shift away from each other and makes the magnetic spiral state ferroelectric.

The magnetically induced ferroelectricity is one of many beautiful phenomena found in frustrated magnetic systems. But as ordering temperatures in frustrated systems are inherently low due to the competition between different spin states, finding a room-temperature multiferroic among these materials is not trivial. Kimura and colleagues have now shown that this is possible[1], provided that spins in frustrated magnets interact strongly, as they do in copper oxides.

High transition temperature is not the only condition necessary for multiferroic materials to be used in devices. The hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ orders magnetically well above room temperature[4]; in a magnetic field it becomes ferroelectric, but its electric polarization can only be reliably measured up to 130 K. The problem is that insulators such as hexaferrite and even CuO become conducting at high temperatures, making it difficult to align electric dipoles by an applied electric field.

Nevertheless, the discovery of high-temperature multiferroic coupling in CuO shows that the potential of geometrically frustrated magnets to generate magnetoelectric phenomena is nowhere near exhausted, and that novel lattice geometries, magnetic

orders and microscopic mechanisms of magnetoelectric coupling leave plenty of room for further discoveries. In that respect, the work of Kimura and colleagues opens a new hunting ground: high-temperature copper oxide multiferroics.

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PEROVSKITE OXIDES

An atomic force pencil and eraser

A method of writing and erasing conducting nanostructures at the interface between the wide-bandgap insulators $LaAlO_3$ and $SrTiO_3$ is presented. New developments for ultrahigh-density information storage look feasible.

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Perovskite oxides exhibit an exceptional range of properties, including high-temperature superconductivity, colossal magnetoresistance and ferroelectricity. Recently, the remarkable properties of the interfaces between layers of different perovskite oxides have expanded the interest of researchers in this class of materials. Notably, studies on single epitaxial connections between the comparatively wide-bandgap insulators $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) have shown the interfaces to be either high-mobility electron conductors or insulators, depending on the atomic stacking sequence at the interface[1]. Interfaces between these non-magnetic materials also exhibit magnetism[2] and even superconductivity[3]. On page 298 of this issue, Cheng Cen and co-authors show the possibility to 'write' and 'erase' conducting wires at the interface between LAO and STO with the tip of an atomic force micropscope (AFM)[4], taking the first step towards highly dense nanodevices.

Cen *et al.* used a positive-biased conducting AFM tip as their writing tool. The tip was scanned over the surface of three unit cells of LAO grown on a TiO_2-terminated STO substrate, starting from a conducting electrode and moving towards a second one (Fig. 1). The conductance between the two electrodes is very low, but as soon as the AFM tip reaches the second one, the conductance increases, demonstrating the creation of a metallic wire. By applying a negative bias voltage at the AFM tip that scans perpendicularly over the wire, the conductance drops again, indicating that the wire has been cut.

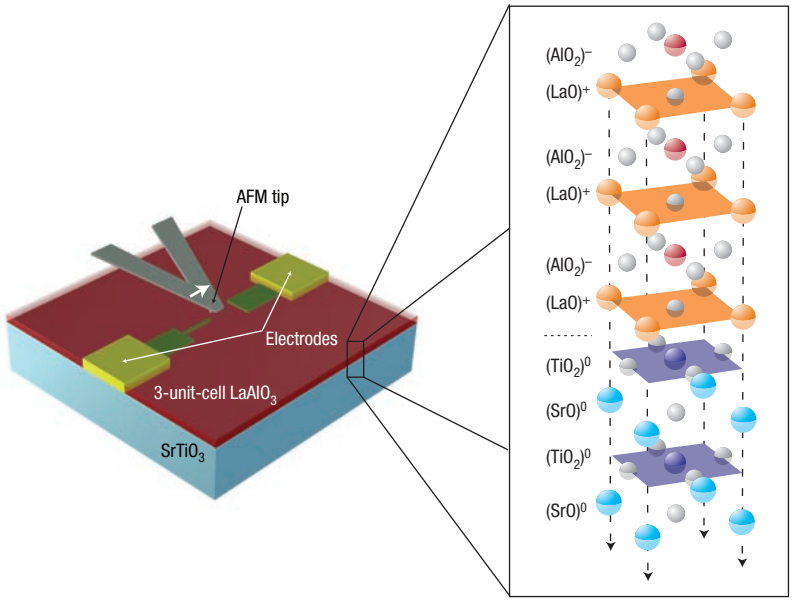

Figure 1 Scheme of the experiment reported by Cen and colleagues[4]. The AFM tip is used almost as a pencil to draw a conducting line between two electrodes on the board represented by the interface between LAO and STO. The white arrow shows the direction of movement of the tip. The right panel shows the layer structure of the device.

The transport properties of the interfaces are closely connected to the number of LAO unit cells grown above the LaO/TiO_2 interface. For example, Huijben *et al.* were able to tune the conductivity by creating the complementary interface with a spacing of less then six unit cells[5]. Thiel *et al.* found that, for the interfaces to be conducting, the number of $LaAlO_3$ unit cells had to reach a critical thickness of four[6]. Just below this critical thickness, Cen *et al.* were able to control the interfacial metal–insulator transition at room temperature using a conducting AFM. Experiments with two or four unit cells did not show the switching effects.

Metal–insulator transitions have been reported earlier in perovskites, such as electrically controlled resistive switching in titanates and manganites[7]. Typically, low-voltage pulses result in a reversible change in resistance, originating from oxygen ion or vacancy incorporation. This effect forms the basis of non-volatile resistance random access memory (ReRAM). Using a conducting AFM as an electrode in a